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# Directed Self-Assembly and Morphology of Aryl-Substituted POSS in Polyetherimide Films

Andrew J. Guenther,<sup>1</sup> Gregory R. Yandek,<sup>1</sup> Kevin R. Lamison,<sup>2</sup> and Joseph M. Mabry<sup>1</sup>

<sup>1</sup>Air Force Research Laboratory, Space and Missile Propulsion Division, Edwards AFB, CA 93524.

<sup>2</sup>ERC, Incorporated, Edwards AFB, CA 93524.

## ABSTRACT

Polyhedral oligomeric silsesquioxanes (POSS) share characteristics of small molecules as well as nanoparticles, making them attractive candidates for studies of directed self-assembly. The use of POSS in high-temperature engineering thermoplastics has been limited to date by strong incompatibility between the generally aliphatic POSS substituents and the generally aromatic backbones of engineering thermoplastics. We report on the morphology (via SEM and light scattering), and physical properties (such as T<sub>g</sub>) of a new class of blends: POSS compounds containing aromatic substituents in the engineering thermoplastic polyetherimide, with a focus on the role of polymer orientation in directing the morphology of POSS aggregation. Since molecular orientation is relatively easy to control in engineering thermoplastics, it represents a potentially useful means of forming controlled nanoscale morphologies that impart beneficial properties such as heat resistance, wear resistance, and decreased permeability to high-performance thermoplastic materials.

## INTRODUCTION

Polyetherimide (PEI) has found widespread use in many high-temperature, microelectronics, and aerospace applications.<sup>1</sup> Recently, nanoscale reinforcement of polymers such as PEI has emerged as a viable route to improved performance.<sup>2</sup> Traditional means of nanoscale reinforcement, such as the addition of carbon nanotubes<sup>3</sup> or Montmorillonite clay<sup>4</sup> particles, have led to significantly improved properties only when effective dispersion of the reinforcing agent has been achieved. Often, achieving such dispersion constitutes a substantial challenge.

A more sophisticated approach to nanoscale reinforcement involves the self-assembly of nanoparticle additives. For instance, nanoparticles arranged into a raft-like form can offer advantages similar to nanoclay,<sup>5</sup> such as improved barrier properties, improved fire resistance, and decreased wear, with simpler processing requirements. Effective self-assembly, however, requires 1) good dispersion of nanoparticles, 2) a means of triggering nanoparticle re-aggregation, and 3) an exploitable means of controlling the aggregation process via a strong interaction.

While smaller nanoparticles are generally more difficult to disperse than large ones via melt processing, they can often be dispersed readily via solution processing. In addition, smaller particles exhibit a higher mobility in the resin and feature a large surface area, thereby maximizing the potential for interactions that can alter the aggregation process. Thus, polyhedral oligomeric silsesquioxanes (POSS), which

are only ~1 nm in size, are suitable for nanoscale reinforcement of high-performance thermoplastics via controlled self-assembly.

To date, most studies of POSS-containing compounds, either as additives or as co-monomers, have focused on POSS cages substituted with aliphatic groups.<sup>6,7</sup> As additives in high-temperature thermoplastics, the POSS cages tend to behave like small-molecule plasticizers, lowering the glass transition temperature. In copolymerized polyimide formulations, though, the individual POSS units can form an ordered lamellar structure at the nanoscale. In some cases, it appears that imparting a preferred orientation to the polymer chains also imparts an orientation to these POSS-containing structures.<sup>6</sup> Thus, block copolymer-like self-assembly, directed by external mechanical forces, has been observed in POSS-containing systems. Octafunctional POSS cages containing terminal imide groups have also been blended with PEI, producing ~100 nm core-shell nanostructures.<sup>8</sup>

Recently, POSS cages containing aromatic substituents have been synthesized at the Air Force Research Laboratory. These POSS compounds offer increased compatibility with high-performance engineering thermoplastics such as PEI along with improved heat resistance. We have been able to create homogeneous mixtures of some of these POSS compounds and PEI through the use of solvent-based processing. Moreover, aggregation of the POSS was easily induced during drying of solution cast films. Since the solution casting process affords the opportunity to introduce molecular orientation via directional blade casting techniques, it also provided a means of potentially controlling the morphology of the aggregates. Thus, we investigated film formation in PEI / aromatic-POSS mixtures in order to explore the potential for directed self-assembly as a means of generating improved physical properties of the system.

## EXPERIMENTAL

Polyetherimide (PEI, Ultem 1000, supplied by GE Plastics) was dissolved in either chloroform (Honeywell HPLC Grade) or 1,4-dioxane (technical grade) at approximately 1 g per 5 mL. Various aromatic POSS compounds including octa-naphthyl-POSS T8, naphthyl-hepta-phenethyl POSS T8, octa-phenethyl POSS T8, and octa-tolyl POSS T8 were also mixed in the same solvents at approximately 1 g per 10 mL. The PEI solution was then added to the POSS solution at a weight ratio of either approximately 3 to 1 (in chloroform) or 6 to 1 (in dioxane), in order to produce a blend solution comprising roughly 10 wt% solids and a POSS to PEI ratio of around 1:7, by weight.

For directional casting, a few drops of the blended POSS/PEI solution were poured onto a clean microscope slide and sheared at a rate of around 5 cm/s using a glass blade with a gap of approximately 0.01 cm. For spin casting, a few drops of the blended solution were poured onto a clean microscope slide and spun using a 10 s ramp to 400 rpm and a sustained 20 s spin at 400 rpm. The solutions were then dried under a glass dish at room temperature.

For differential scanning calorimetry (DSC) analysis, the blended solutions were poured into aluminum DSC pans and dried overnight, then analyzed in a TA Instruments Q200 differential scanning calorimeter under a 50 mL/min nitrogen purge, using heating and cooling rates of 10°C/min.

Two-dimensional small angle light scattering (SALS) by our fabricated films was captured with home-

made instrumentation featuring a laser diode ( $\lambda=635$  nm) and a CCD camera. SEM images were obtained using a FEI Quanta 600 scanning electron microscope at 15 kV in low-vacuum mode on cross-sections produced by mounting the films in a thin layer of epoxy and cryofracturing.

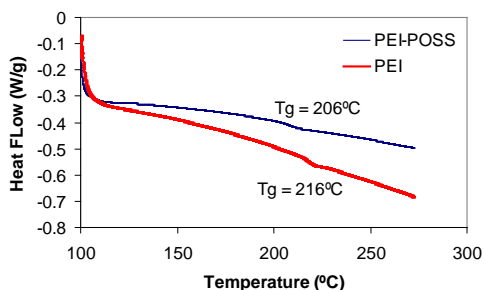
## RESULTS

**Solubility.** As seen in Table 1 (“+” indicates solubility) only the phenethyl POSS was completely soluble in a suitable blend solution, using either dioxane or chloroform as the POSS carrier solvent. The tolyl and naphthyl-hepta-phenethyl POSS materials could be dissolved in chloroform, but were insoluble in solutions containing a significant amount of dioxane, thus only PEI cast from chloroform could be used for blend films. PEI films cast from solutions containing only chloroform gelled within a few seconds of deposition and formed poor quality films, thus additional study was limited to phenethyl POSS / PEI films.

**Table 1. Solubility of POSS Compounds**

| POSS Compound                                  | Solubility in...  |             |             |
|--|-------------------|-------------|-------------|
|  | CHCl <sub>3</sub> | 1,4-dioxane | Casting Mix |
| 1-naphthyl <sub>8</sub> T <sub>8</sub>         | -                 | -           | n/a         |
| 1-naphthyl-phenyl <sub>7</sub> -T <sub>8</sub> | +                 | +           | -           |
| phenethyl <sub>8</sub> T <sub>8</sub>          | +                 | +           | +           |
| tolyl <sub>8</sub> T <sub>8</sub>              | +                 | +           | -           |

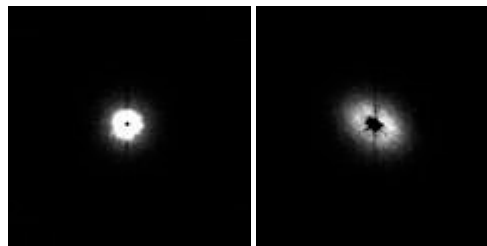
**Glass Transition..** Figure 1 shows that the glass transition temperature of the phenethyl POSS-containing PEI at about 13 wt% decreased by about 10°C compared to PEI films cast using the same procedures. The observed T<sub>g</sub> of PEI of 216°C is in line with the reported values for the pure polymer.<sup>1</sup>



**Figure 1.** DSC of PEI with and without 13 wt% octa-phenethyl-T<sub>8</sub> POSS

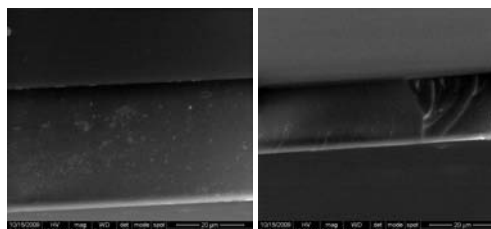
**POSS Morphology.** The light scattering patterns evolved from the spun-cast (left) and directionally-cast (right) phenethyl POSS/PEI solutions are shown in Figure 2. Both patterns indicate a measurable degree of phase separation with greater development of concentration fluctuations in the spun-cast film concomitant with collapse of the scattered radiation to zero. The phase separated domains demonstrate orientation in the directionally-cast film as evidenced by the skewed scattering ring on the image at right.

Further confirmation of the effect of processing on POSS morphology is provided by the SEM micrographs shown in Figure 3. The cross-section of the POSS/PEI film formed via spin casting (left) exhibits significantly larger aggregates than the film formed via directional blade casting (right). Although a faster drying time for the blade cast film may also play a role, the results clearly show that films with identical compositions cast



**Figure 2.** Scattering patterns from (left) spun-cast phenethyl POSS/PEI film and (right) directionally-cast film of equivalent composition.

from the same solution can exhibit very different morphologies. In particular, with directional casting, it may be possible to impart a nanoscale morphology.



**Figure 3.** Cross-sectional SEM of spun-cast phenethyl POSS/PEI film (left) and directionally-cast film of equivalent composition (right).

## CONCLUSIONS

Of the aromatic POSS compounds investigated, only octa-phenethyl POSS was successfully blended into PEI via solution casting. The incorporation of phenethyl POSS modestly lowered the glass transition temperature, suggesting that, like aliphatic POSS, it acts as a plasticizer. The film casting process was shown to have a significant effect on POSS morphology, affording the possibility for nanoscale reinforcement of PEI via directed self-assembly.

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